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## (54) POLYOXYETHYLENE GLYCOL DIHALIDES

(71) We, GAF CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America, having its main office at 140 West 51st Street, New York, New York 10020, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention provides a mixture of polyoxyethylene dihalides, each of every component of the mixture having the general formula:

$$XCH_2—CH_2—(—OCH_2—CH_2—)_n—OCH_2—CH_2X$$

in which $n$ is an integer of from 3 to 600, X is halogen and the mixture has an average molecular weight between 275 and 30,000.

Preferred halogens for X are chlorine or bromine and for most end uses it is preferred that the integer $n$ in the above formula is from 7 to 14. For most uses it is also preferred that the average molecular weight of the mixture of the invention be from 450 to 850.

The mixtures of the inventions are useful for a wide variety of purposes, including but not limited to use as solvents, reaction media, surface-active agents and reactive intermediates. Since these mixtures are hydrophilic they are also useful for purposes such as hydrophilic blocks for condensation block polymers and hydrophilic block cross-linking agents for preformed functional polymers. The mixtures of the invention, especially the preferred mixtures, are especially useful as surfactants where their low cost and low foaming characteristics render them especially valuable.

It is an essential characteristic of the compounds of the invention that the integer "$n$" in the above formula is at least 3. If $n$ is less than 3, the desired polymer characteristics will not be obtained. For instance, mixtures of the invention in which $n$ is equal to or greater than 3 display marked surface-active characteristics whereas mixtures of similar structure wherein $n$ is less than 3 do not display such characteristics. Likewise, mixtures of the invention are signficantly more soluble in water than the basically monomeric materials represented by similar structures in which $n$ is less than 3.

Mixtures of the invention may be prepared by suitable means such as by reacting polyethylene glycols with a slight excess of 2 molar quantities of thionyl halide. The compounds of the present invention where X= iodine may also be prepared from the corresponding chlorides or bromides by treating with alkali metal halides such as sodium iodide.

The following examples illustrate representative and preferred embodiments of the invention and the preparation and use thereof.

### Example 1

In this example a preferred mixture of the invention is prepared by heating 400 grams of polyethylene glycol, having an average number molecular weight of 400, with 300 grams of thionyl chloride at such a rate that the temperature of the reaction mixture does not exceed 55°C. During addition of thionyl chloride, considerable amounts of gas, mostly HCl and $SO_2$ are evolved. When addition of thionyl chloride is complete the reaction mixture is heated to 100°C and dry air allowed to bubble through the mixture for about 15 minutes during which the temperature of the mixture is held between 100 and 110°C. The dark brown reaction product is then heated with 30 grams of soda ash to remove unescaped HCl and/or excess thionyl chloride, filtered and bleached at 100—110°C with 25 grams of 30% hydrogen peroxide for 15 minutes. The product is then dried by blowing dry air for 15 minutes at 100—110°C. The dark dichloride product,

$$ClCH_2CH_2—(—OCH_2CH_2—)_n—OCH_2CH_2Cl$$

is found to have an average molecular weight of 437 and may be recovered in an amount of 435 grams. Organically bound chlorine in this product is 16.2% and infra red analysis indicates absence of any hydroxyl groups. The product has a viscosity of 30 centipoises (cps). This compares with a viscosity of 85 cps for the polyethylene glycol starting material.

Example 2

Using the procedure of Example 1 with 300 grams of polyethylene glycol of an average molecular weight of 300 as starting material, corresponding dichloride may be recovered in yields exceeding 90%. The product has a solubility of 8% in water at 20°C.

Example 3

The procedure of Example 1 is repeated but with soda ash treatment omitted. Yield is 435 grams and the product in other respects is identical with that obtained from Example 1.

Example 4

The procedure of Example 3 is repeated using as starting material 600 grams of polyethylene glycol having an average molecular weight of 600. Yield of the dichloride product is 630 grams and the product has an average molecular weight of 637.

Example 5

In addition to the mixtures mentioned above, other suitable mixtures of the invention include the mixtures indicated in Table I below by reference to halogen and numerical value of *n*. It is to be understood that in each case the generic formula given above in the summary of the invention is the formula representing the mixture and that the mixture has the halogen and numerical value for *n* indicated in Table I. It is understood that in these mixtures as in other mixtures discussed herein the numerical value for the integer *n* leads to an average molecular weight value between 275 and 30,000.

TABLE I

Suitable halides for use in forming mixtures of the invention include, for instance, the following:

| Mixture No. | Halogen | Numerical Value of n |
|---|---|---|
| 1 | Br | 100 |
| 2 | F | 500 |
| 3 | I | 10 |
| 4 | Cl | 3 |
| 5 | Cl | 35 |
| 6 | Br | 150 |
| 7 | Br | 75 |
| 8 | I | 300 |
| 9 | F | 400 |
| 10 | Cl | 20 |

Example 6

This Example illustrates the utility of mixtures of the invention as surfactants. In this Example surface tension is measured for various concentrations of the product as Example 1 in water with the results shown in Table II.

TABLE II

Surface Tension

| Concentration of Product from Example 1 in Water | Surface tension dynes/cm |
|---|---|
| 0.0 (Control) | 74.0 |
| 0.01 | 50.5 |
| 0.02 | 48 |
| 0.05 | 45.1 |
| 0.10 | 40.2 |
| 0.11 | 40.2 |
| 1.00 | 39.2 |
| 10.00 | 35.8 |

The above surface tension data shows that the product from Example 1 has good surface-active properties in the sense that it significantly lowers the surface tension of water even when present in small quantities. When a concentration *vs.* surface tension graph is plotted, it is found that the points in general fall in two straight lines which intersect at a point whose co-ordinates correspond to 0.11% concentration and 40.0 dynes/cm. Thus CMC of this surfactant (Example 1) is 0.11% and the surface tension at CMC is about 40 dynes/cm. (CMC=critical micellar concentration).

Example 7

This Example shows that the product of Example 1 shows a cloud point phenomenon, a phenomenon often common to many nonionic surface-active agents. When an aqueous solution of a nonionic surface active agent is heated, it turns turbid at certain temperatures and on further heating causes the surface-active compound to separate from the aqueous solution. The temperature at which the solution starts to become turbid is known as the cloud point. A 10% solution of the product of Example 1 shows a cloud point of 50—54°C.

WHAT WE CLAIM IS:—

1. A mixture of polyoxyethylene dihalides, each or every component of the mixture having the general formula:

$$XCH_2—CH_2—(—OCH_2—CH_2—)_n—OCH_2—CH_2X$$

in which *n* is an integer of from 3 to 600, X is halogen and the mixture has an average molecular weight between 275 and 30,000.

2. A mixture according to Claim 1, in which X is chlorine or bromine.

3. A mixture according to Claim 1 or Claim 2 in which *n* is an integer of from 7 to 14

and the mixture has an average molecular weight of 450 to 850.

4. A mixture according to Claim 1 substantially as herein described and exemplified.

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